

**REMARKS**

Claims 1-39 are pending in the present application and were rejected on various grounds in the Office Action mailed on January 30, 2004. Applicants appealed and the rejections were upheld by the Board in a Decision mailed on November 7, 2005 and a Decision on Request for Rehearing mailed on February 23, 2006.

Claims 1 and 36 are amended herein to specify that the ALD reactions take place at a temperature of 150 to 400°C. Claims 1 and 27 have been amended to indicate that amorphous films are deposited. Claim 28 has been amended to indicate that the deposition temperature is from 100 to 400°C. The amendments are fully supported by the specification and claims as originally filed, for example at page 4, lines 22-23 and page 8 line 31 through page 9, line 4. No new matter is added by the amendments.

**Claim Rejections Under 35 U.S.C. §103**

Claims 1-39 stand rejected under 35 U.S.C. §103(a) as unpatentable over DiMeo (U.S. Patent No. 5,972,430) in view of Kirlin (U.S. Patent No. 5,453,494) and/or Maiti (U.S. Patent No. 6,020,024). In particular, the Examiner found that DiMeo discloses a CVD method for forming multi-component oxide layers and that DiMeo describes ALE as an equivalent variant of CVD. While DiMeo does not teach or suggest cyclopentadienyl precursors, this deficiency was found to be made up for by Kirlin.

The oxide thin films produced by the claimed methods do not grow epitaxially and the films are annealed after deposition in order to obtain the desired crystallinity. Examples 1-3 each discuss annealing at a temperature of 500°C to improve crystallinity. In order to clarify this feature, independent Claims 1 and 27 have been amended to indicate that amorphous films are deposited by the recited ALE methods. In addition, Claims 1 and 36 have been amended to specify that the atomic layer deposition reactions take place at a temperature of 150 to 400°C, while Claim 28 has been amended to indicate that deposition takes place at a temperature of 100 to 400°C. These temperature ranges are low enough that epitaxial deposition does not occur.

Applicants note that the use of the term “atomic layer epitaxy (ALE)” in the present claims does not indicate that the films are epitaxially deposited. While thin films can be deposited epitaxially by ALE, this is not always the case and is not implied by the use of the term

Appl. No. : 09/787,062  
Filed : June 28, 2001

"ALE." Rather, the term "epitaxy" was originally used in the term "ALE" to indicate that the films are "arranged" on top of one another, as described in an article by the principal inventor of ALE, Dr. Tuomo Suntola in the article "Atomic Layer Epitaxy" on page 266, first paragraph (T. Suntola, 1989, "Atomic Layer Epitaxy," Elsevier Science Publishers, Amsterdam, pp 261-309, excerpt attached). More recently, the term ALE has been replaced with the term atomic layer deposition (ALD), which more accurately reflects the fact that epitaxial deposition is not necessarily achieved. Again, the fact that claimed methods do not provide for epitaxial deposition is confirmed by the present specification, which discloses deposition of amorphous films (pages 8-9, carryover paragraph) and subsequent annealing to improve crystallinity (Examples 1-3).

On the other hand, it is clear that DiMeo *is* focused on truly epitaxial deposition processes. For example, at column 3, lines 44-46 and column 4, lines 1-12, DiMeo states that one of the objects of their invention is to improve oxide properties by enhancing crystallinity. Enhanced epitaxial deposition is also referred to at column 6, lines 17-29 and is inherent in the formation of high k films (column 7, lines 8-11). Further, DiMeo does not teach or suggest a post-deposition anneal to improve crystallinity. Thus, to the extent that the passage cited by the Examiner and the Board in support of the current rejection suggests an ALE process ("chemical vapor deposition (CVD) methods and related *epitaxial* deposition methods, such as but not limited to atomic layer epitaxial (ALE) deposition methods, are in turn presently of substantial interest"), the suggestion is limited to *true epitaxial* ALE processes. There is no teaching or suggestion related to non-epitaxial deposition processes. In addition, because DiMeo is concerned with epitaxial deposition, one of skill in the art would not be motivated to optimize the film deposition temperature in the claimed range, as it would lead to non-epitaxial deposition and thus run counter to DiMeo's stated goals.

Consistently, the deposition temperatures disclosed in DiMeo are high enough that the films grow truly epitaxially (as crystalline films) on the substrate and no post-deposition annealing is required. As a result, there is no teaching or suggestion in DiMeo of atomic layer deposition reactions at the claimed temperature range or that would produce amorphous films.

Applicants' recited temperature range is unobvious over DiMeo because it would not have been considered appropriate for epitaxy. DiMeo has no teaching or suggestion of atomic layer deposition processes at the claimed temperature range or of deposition of amorphous films.

Appl. No. : 09/787,062  
Filed : June 28, 2001

Furthermore, there is no indication in any of the asserted references that the recited precursors would be useful at the recited temperatures. These deficiencies are not made up for by any of the secondary references. Accordingly, Applicants request that the present rejection be withdrawn.

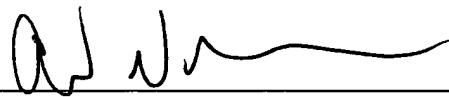
### CONCLUSIONS

In view of the present amendments and arguments, Applicants submit that the pending claims are in condition for allowance. If some issue remains that the Examiner believes can be addressed by Examiner's Amendment, he is cordially invited to telephone the undersigned for authorization.

Respectfully submitted,

KNOBBE, MARTENS, OLSON & BEAR, LLP

Dated: April 24, 2006

By:   
\_\_\_\_\_  
Andrew N. Merickel  
Registration No. 53,317  
Attorney of Record  
2040 Main Street  
Fourteenth Floor  
Irvine, CA 92614  
(415) 954-4114

W:\DOCS\ANM\ANM-5303.DOC  
052803



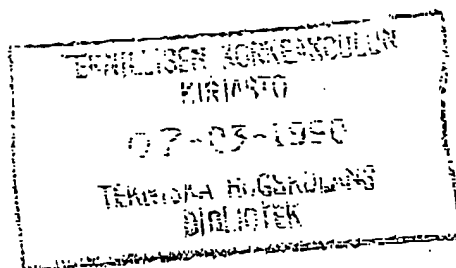
261

## ATOMIC LAYER EPITAXY

Tuomo SUNTOLA

*Microchemistry Ltd., Box 45, SF-02151 Espoo, Finland*

Received 19 February 1989; in final form 15 April 1989



S51737



1989  
NORTH-HOLLAND - AMSTERDAM



## Contents

1. Introduction	2
2. The mechanism of the ALE process	2
2.1. Elemental reactants	2
2.1.1. Formation of a monolayer of element A	2
2.1.2. Purge time	2
2.1.3. Formation of a monolayer of element B	2
2.2. Compounds as the reactants	2
2.2.1. Metal halides and hydrides as reactants	2
2.2.2. Formation of a metal halide monolayer	2
2.2.3. Saturation of a metal halide monolayer	2
2.2.4. Reaction between a metal halide surface and a hydride reactant, formation of a monolayer B	2
2.2.5. Organometallic compounds as reactants	2
2.2.6. Monolayer formation	2
2.2.7. Re-evaporation of a monolayer during a purge sequence, effects of residual gas interaction	2
2.2.8. Reaction between a metal or a metal compound monolayer and a non-metal or a non-metal hydride	28
2.3. ALE process for elemental materials	28
2.4. The processing window of ALE	28
3. Equipment for the ALE process	28
3.1. System classification, open and closed systems	28
3.2. Vacuum systems	28
3.3. A lateral flow system with inert-gas valving	28
3.4. Inert-gas systems with moving substrate	28
4. Experimental	28
4.1. Gallium arsenide	28
4.1.1. Pioneering work on a TMG + AsH <sub>3</sub> process	28
4.1.2. Introduction of a GaCl + AsH <sub>3</sub> process	28
4.1.3. A model of photocatalysis in a TMG + AsH <sub>3</sub> process	28
4.1.4. Further development of ALE processes of GaAs	28
4.1.5. Processes based on TMG + AsH <sub>3</sub>	29
4.1.6. Triethylgallium as a replacement for TMG	29
4.1.7. Gallium chloride (diethylgallium chloride) + arsine	29
4.1.8. Surface migration under ALE growth conditions	29
4.2. Other III-V compounds	29
4.2.1. AlAs	29
4.2.2. InP, GaP and InAs	29
4.2.3. Heterostructures of III-V compounds	29

<i>Atomic layer epitaxy</i>	263
4.3. II-VI single crystals	300
4.3.1. CdTe	300
4.3.2. ZnSe and ZnTe	301
4.3.3. ZnS	302
4.4. II-VI thin films, oxides and nitrides	302
4.5. ALE electroluminescent devices	304
4.5.1. ALE-EL thin film structure	304
4.5.2. ALE-EL devices	307
5. Summary	307
Acknowledgements	308
References	309

## ATOMIC LAYER EPITAXY

Tuomo SUNTOLA

*Microchemistry Ltd., Box 45, SF-02151 Espoo, Finland*

Received 19 February 1989; in final form 15 April 1989

This review discusses the development and present status of atomic layer epitaxy (ALE), a technology for growing layers of crystalline and polycrystalline materials one atomic layer at a time. Atomic layer epitaxy was originally developed to meet the needs of improved ZnS thin films and dielectric thin films for electroluminescent thin film display devices. Accordingly, early work on ALE was mainly carried out for thin films. During the 80s there has been a growing interest in applying ALE in the growth of single crystals of III-V and II-VI compounds and ordered heterostructures such as layered superalloys and superlattices. ALE has also been extended to the growth of elemental single crystals. A basic advantage of atomic layer epitaxy is in the increased surface control of the growth. This is achieved by combining a sequential reactant interaction with a substrate at a temperature which prevents condensation of individual reactants on the growing surface. This results in a stepwise process where each reactant interaction is typically saturated to a monolayer formation. Accordingly, the rate of the growth in an ALE process is determined by the repetition rate of the sequential surface reactions, and the thickness of the resulting layer is determined by the number of reactant interaction cycles. This self-controlling feature of atomic layer epitaxy ensures excellent uniformity of the thickness over large substrate areas even on non-planar surfaces. Owing to its principle of operation, ALE is especially suitable for producing layered structures of III-V and II-VI compounds. Superlattice structures of both these material groups have already been demonstrated. As a limiting case of superlattices, layered superalloys have also been grown. In ALE, chemical reactions producing a material, are divided into separate subreactions between a vapor and a solid surface, each of which results in a new atomic layer of the material. From the theoretical point of view ALE offers a unique link between theoretical and experimental chemistry by permitting direct observations of subreactions under conditions where the chemical environment is more precisely determined than in conventional continuous reactions.

## 1. Introduction

Atomic layer epitaxy is a method for producing thin films and layers of single crystals one atomic layer at a time utilizing a self-control obtained through saturating surface reactions. In conventional terminology, the term "epitaxy" has been used to describe the growth of single-crystal layers. An extension of the term epitaxy to also cover thin films in the case of atomic layer epitaxy is motivated through the original meaning of the expression "epitaxy". It comes from the Greek language and means "on arrangement". In ALE, a controlled "on arrangement" of atomic layers is obtained by sequentially controlled surface conditions.

Atomic layer epitaxy was originally developed to meet the needs of improved ZnS thin films and dielectric thin films for electroluminescent thin film display devices [1-3]. This goal was met, and it led to the commercial production of electroluminescent devices by Lohja Corporation in Finland. Because of this practical goal, the early development of atomic layer epitaxy was directed towards thin film processes which utilized large substrates. The selection of materials was limited to a few II-VI compounds and oxides. Scientific work on the mechanism of the growth was limited to the needs of practical processing of the thin films mentioned.

The basic mechanism of ALE, saturation of a monolayer onto the surface and a rate of growth that is proportional to the number of reaction cycles instead of to the time of the growth and the intensity of the material flux, was first proved simply by observing the growth per cycle with different dosing at different temperatures [1].

ALE is based on separate surface reactions between the growing surface and each of the components of the compound, one at a time. The components of the compound are supplied to the growing surface in vapor phase, either as elemental vapors or as volatile compounds of the elements. As a general introduction to the ALE process, fig. 1 summarizes the basic sequences of ALE in two alternative ways of producing ZnS. In each reaction there are sites for only one monolayer to make a bond with the original surface. A basic condition for a successful ALE

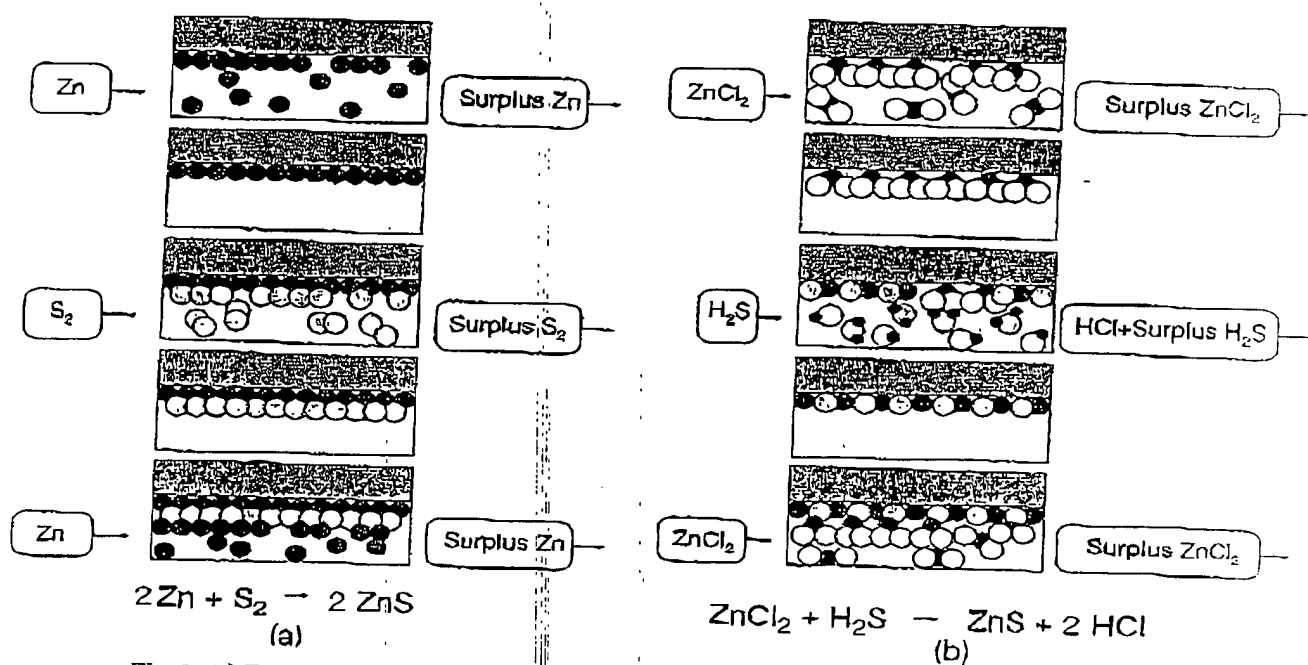


Fig. 1. ALE process for ZnS. (a) Zn and S as the reactants, (b) ZnCl<sub>2</sub> and H<sub>2</sub>S as the reactants.



*Atomic layer epitaxy*

267

Table 1

Laboratories working on ALE, according to published papers. The list has been ordered according to the date of the first published paper of each laboratory. Laboratories marked with an asterisk have not reported ALE processing, but describe the analysis of ALE thin films or single-crystal layers carried out in other laboratories

No.	Laboratory	Ref.
1	Lohja Co., Espoo, Finland	[1-9]
2	Tampere University of Technology, Tampere, Finland	[10-19]
3*	Helsinki University of Technology, Laboratory of Physics, Espoo, Finland	[20-34]
4*	Akademie der Wissenschaften der DDR, Zentralinstitut für Elektronenphysik, Berlin, DDR	[35]
5*	Institut für Festkörperphysik der Technischen Universität Berlin, Berlin, Germany	[36]
6*	Siemens AG, Munich, FRG	[37]
7	Helsinki University of Technology, Department of Chemistry, Espoo, Finland	[38-51]
8*	Joensuu University, Joensuu, Finland	[52-54]
9	Tohoku University, Sendai, Japan	[55-57]
10	{ Electrotechnical Laboratory, Ibaraki, Japan Tokai University, Kitakaname, Hiratsuka, Kanagawa, Japan	[58-68]
11	North Carolina State University, Raleigh, NC, USA	[69-78]
12	Research Development Co. of Japan, Semiconductor Research Institute, Sendai, Japan	[79-88]
13*	Standard Telecommunication Laboratories Ltd., Harlow, Essex, UK	[89,90]
14	NEC Co., Kawasaki, Japan	[91-105]
15	NTT Electrical Communications Laboratory, Musashino-shi, Tokyo, Japan	[106-115]
16	{ The Institute of Physical and Chemical Research, RIKEN, Saitama, Japan Hosei University, Tokyo, Japan Waseda University, Tokyo, Japan	[116-126]
17	Fujitsu Laboratories Ltd., Atsugi, Japan	[127-132]
18	Laboratoire Matériaux Exploratoire, L.C.R., Thomson C.S.F., Orsay, France	[133]
19	Rockwell International Science Center, Thousand Oaks, CA, USA	[134]
20	University of Southern California, Los Angeles, CA, USA	[135-138]
21*	The Wolfson Institute for Surface Engineering, Leeds University, Leeds, UK	[139]
22	Massachusetts Institute of Technology, Cambridge, MA, USA	[140]
23	McMaster University, Hamilton, Ontario, Canada	[141]
24	Tokyo Institute of Technology, Tokyo, Japan	[142-145]
25	Tokyo University of Agriculture and Technology, Tokyo, Japan	[146]
26	Philips Research Laboratories, Eindhoven, The Netherlands	[147]
27	Institut für Experimentalphysik, Johannes Kepler Universität, Linz, Austria	[148-150]
28	Hokkaido University, Sapporo, Japan	[151]
29	Changchun Institute of Physics, Changchun, China	[152]
30	Bell Communications Research Inc., Red Bank, NJ, USA	[153,154]
31	Purdue University, West Lafayette, IN, USA	[155]

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☒ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**